

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :	A1	(11) International Publication Number: WO 98/30599
C08F 2/42, 10/00		(43) International Publication Date: 16 July 1998 (16.07.98)

(21) International Application Number: PCT/US98/00553	(81) Designated States: BR, CN, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 13 January 1998 (13.01.98)	
(30) Priority Data: 60/034,488 13 January 1997 (13.01.97) US 09/006,382 12 January 1998 (12.01.98) US	Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US).	
(72) Inventors: AN, Ui, Sun; 2810 Judson Road #1208, Longview, TX 75605 (US). DOOLEY, Kenneth, Alan; 402 Northwest Drive, Longview, TX 75604 (US). DUCKWORTH, Brad, Thedford; 210 Joan, Longview, TX 75605 (US). FORD, Randal, Ray; 3013 Latonia, Longview, TX 75605 (US). MOORE, Glenn, Edward; 110 Oak Isle Drive, Longview, TX 75605 (US). RAMSEY, Dennis, Olin; 824 Noel Drive, Longview, TX 75602 (US).	
(74) Agent: GRIFFIS, Andrew, B.; P.O. Box 511, Kingsport, TN 37662-5075 (US).	

(54) Title: TEMPORARY IDLING OF A POLYMERIZATION REACTION

(57) Abstract

Disclosed is a method for idling a polymerization reaction. The method injects a sufficient amount of deactivating agent to deactivate the catalyst while allowing the reaction to be re-established simply by adding fresh catalyst. The idling method allows for maintaining polymerization reaction conditions during a shutdown and significantly reduces the amount of time associated with re-establishing polymerization reaction conditions.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

- 1 -

TITLE OF THE INVENTION

**TEMPORARY IDLING OF A POLYMERIZATION REACTION**

5

CROSS-REFERENCE TO RELATED APPLICATIONS

This Application claims the benefit under 35 U.S.C. § 119(e) of Provisional Application Serial No. 60/034,488, filed January 13, 1997, and incorporated herein.

10

FIELD OF THE INVENTION

The present invention relates to a process for idling a polymerization reaction by addition of a catalyst deactivator.

15

BACKGROUND OF THE INVENTION

It is well known that polymers can be produced by olefin polymerization in a fluidized bed gas phase reactor. Typically, a reaction gas mixture containing the olefin(s) being polymerized is passed upwardly through the reactor, and the newly formed polymer particles are kept in a fluidized state. The gas mixture exits the top of the reactor and is recycled back to the bottom of the reactor by a compressor. The heat absorbed by the gas mixture during polymerization is removed by heat exchangers. Examples of a fluid bed polyolefin process are disclosed in U.S. Patent No. 4,882,400 and U.S. Patent No. 5,332,706. Numerous configurations and modifications are known.

It is generally undesirable to shut down a polymerization reaction. However, there are sometimes overriding reasons for shutting down such a

process. For instance, during the commercial operation of a gas phase polymerization process, instances that pose a significant risk to the continuous operation of the fluidized bed reactor may arise. For example, if the compressor used for the gas loop cooling and recycling fails, due to electrical or mechanical failure, the cooling in the bed is lost and the exothermic reaction increases the temperature of the bed to sintering temperatures in a run-away fashion, as described in U.S. Patent No. 4,547,555 (note, e.g., column 1, lines 66-68). This circumstance warrants an emergency shut down of the reactor.

In addition, the continuous operation of a fluidized bed reactor is often jeopardized by operational problems. For example, U.S. Pat No. 4,306,044 describes the importance of rapidly reducing the rate of reaction during a runaway reaction (e.g., column 1, lines 15-30). Runaway reactions in fluidized bed reactors can result in the fusing of the polymer into large agglomerate chunks which can be very difficult to remove.

Another potential risk to the continuous operation of a fluidized bed reactor is the mechanical problems that may arise with the polymer withdrawal system. The withdrawal system removes polymer from the reactor at a rate equal to the production of polymer in the reactor, such that the bed level of the fluidized bed is maintained at a constant level. During a withdrawal system failure, polyethylene powder cannot be removed from the reactor. Since no polymer is removed from the reactor, the bed level in the reactor could elevate high enough for the bed to carryover into the gas loop recycle line. The carryover poses serious risks to the operation and life of the heat exchangers and compressor in the recycle gas loop.

Also, reactor transitions present a problem. Reactor transitions are scheduled discontinuous operations of the reactor. A fluidized bed reactor undergoes transitions to change polymerization reaction conditions in order to produce different products with different properties. To accomplish an effective

transition of different target reactor operating conditions, it is preferable that the existing active catalyst sites in the reactor be deactivated. By deactivating the active catalyst sites, the production of transition material is reduced. Bringing the system back to full operation is very time consuming.

5 Various strategies are known for shutting down a reactor. For instance, catalyst or reactant feed can be stopped. However, stopping the feeds to the reaction process will not stop polymerization immediately if all other process parameters, such as temperature, pressure, reactor gas composition, reactor gas velocity, etc., are held constant, since there is still active catalyst and reactants in  
10 the reactor. Such a deactivation can last for a considerable amount of time.

Changing the process parameters, such as by venting of the reactor, can be an effective method, but it is time consuming to reestablish the proper reactor conditions and is economically wasteful.

It is also known to provide a "kill" agent, i.e., to deactivate the catalyst  
15 by adding a catalyst poison. U.S. Pat No. 4,306,044 discloses a carbon dioxide kill system that is used to kill the active catalyst sites in the reactor by injecting carbon dioxide in amount five times the total effective catalyst system (on a molar basis; note, e.g., column 6, lines 47-49). However, this method requires a significant amount of time to vent off excess poison gas and reestablish  
20 polymerization reaction conditions and fails to provide an economic solution.

Also, U.S. Pat No. 4,834,947 discloses the introduction of a carbon oxide gas (CO and CO<sub>2</sub>) and venting gas from the top of the reactor (note, e.g., column 3, lines 14-19). This method also requires a significant amount of time to reestablish polymerization reaction conditions and requires the replacement of  
25 expensive hydrocarbons lost from venting the reactor.

In addition, U.S. Pat. No. 5,270,408 (note, e.g., column 7, lines 28-30 and column 7, lines 59-63) discloses a kill method that also requires the replacement of expensive hydrocarbons lost from venting the reactor contents.

As discussed above, there are remedies that quickly kill the active catalyst sites in a reactor, but suffer various drawbacks, such as they are too slow to deactivate the system, they are uneconomical because they lose reactor contents, and/or require a significant amount of downtime to re-establish reactor 5 conditions. Accordingly, there is a need to temporarily idle a reactor such that the reaction is suppressed while yet maintaining the polymerization reaction conditions in the reactor so that polymerization can commence when desired.

#### SUMMARY OF THE INVENTION

10

The process according to the present invention entails a method for temporarily idling a polymerization process by injecting into the reaction medium a predetermined amount of idling agent so that only catalyst sites currently active are deactivated and so that no free idling agent is present in the reactor. With the 15 active catalyst sites deactivated, polymerization gas compositions, reactor temperature and pressure can be maintained at target conditions or be adjusted to greatly revised target conditions while polymerization is in idle mode. The reaction can then be immediately reestablished when desired, since the reaction gas composition, temperature, pressure, bed fluidization, etc., are controlled at 20 target conditions. The process is more particularly concerned with idling a fluidized gas phase reactor process.

Thus, it is an object of the present invention to provide a method of immediately halting a continuous polymerization process by introduction of a catalyst deactivator, without the requirement of altering the temperature, 25 pressure, or bed fluidization conditions and without venting.

It is another object of the invention to provide a method of immediately reestablishing a continuous polymerization process simply by introducing fresh catalyst and/or co-catalyst(s) into the reactor, thus eliminating the downtime

- 5 -

associated with reestablishing reactor conditions.

These and other objects, features, and advantages of the present invention will become apparent as reference is made to the following drawing, detailed description, preferred embodiments, and specific examples.

5

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows one useful arrangement of a fluid bed polyolefin process.

10

#### DETAILED DESCRIPTION OF THE INVENTION

In the process according to the present invention, an idling agent is added to the reactor to reduce the reaction rate very quickly or stop the reaction altogether by deactivating the catalyst and/or co-catalyst. "Idling agent" as used herein means a catalyst poison, catalyst deactivator, or kill agent, as these latter three terms are *per se* known in the art. The terms are used interchangeably herein unless otherwise specifically noted. More particularly, the idling agent is added to the process in a controlled fashion such that only catalyst sites currently active are deactivated. It is not necessary to alter any other process conditions, although it is preferred that fresh catalyst feed be either reduced or discontinued, depending on how long a downtime is desired. Reactor parameters can be adjusted in the case of a reactor transition. The invention has the advantages of allowing the reaction to be immediately re-established when desired since the reaction gas composition, temperature and pressure are controlled at target conditions while the polymerization is being held in idle mode.

The temporary idling of the reactor is obtained without modifying the normal polymerization reactor operating conditions. By "temporary idling of the reactor" or "temporary idling of the reaction" is meant that the reaction occurring

in the reactor is slowed down to the extent necessary to cure a desired problem or for reactor transition, such as for the reasons discussed above in the introduction.

In some cases it may be desirable to shut down the reaction only to a small extent, for instance only about 50% of the normal rate, but more preferably the 5 reaction is shut down at least 85% from the rate of normal production, even more preferably shut down 98% (i.e., to a rate 2% of the normal rate of production). Ideally the reaction is shut down 100%, but it should be noted that at least one of the critical aspects of the present invention is that no more than 100 % of the idling agent needed is added, since what is desired is for the reaction to be re-established immediately when desired. The presence of excess idling agent will 10 not permit this immediate re-establishment. Therefore, the present inventors have discovered that, as a practical matter to insure that no excess idling agent is add, the idling agent is added in less than the stoichiometric amount required to deactivate the active sites on the catalyst. In addition, the present inventors have found that, as a practical matter, generally absolute shut-down of the reactor is 15 not necessary to cure the reactor problem or make the reactor transition. As mentioned, generally the reaction is idled to the extent of about 50% to 99% (i.e., the rate is now 50% to 1% of the original rate).

The shut down can be achieved solely by addition of the idling agent and, 20 in processes including continuous addition of fresh catalyst, stopping the addition of fresh catalyst. The phrase "solely by addition of fresh catalyst" means that none of the other process parameters, e.g., temperature and pressure, need to be changed. Of course, after the desired reduction in the process is achieved, it may be desirable to change such parameters, e.g., in the case of reactor transitions.

25 The present process permits idling of the reactor by maintaining reactor pressure, bed fluidization, and without venting off the contents of the reactor. In the case where it is desirable to change reactor conditions, such as during reactor transitions, the process according to the present invention permits a more efficient

means of doing so, i.e., by idling the reactor.

The effective reduction of reaction achieved by the current invention varies depending on the fluidized bed level, the active catalyst concentration in the reactor, and the amount of idling agent added. The reduction of reaction is 5 from 50% to about 99%, preferably above 85% and more preferably reaches 98%. Generally, the reactor is shut down so that there is a substantial reduction of the reaction. By "substantial reduction" is meant less than 100 % shut-down, but enough to cure the problem or provide for reactor transitions. This compares with the complete shut down in other reactor kill methods, based on 10 overwhelming the catalyst with kill agent or depressurizing, as discussed above. For example, the degree of polymerization reduction is observed by a low temperature differential of the gas over the inlet and outlet of the reactor 9 (referred to as "reactor bed temperature differential"), which in the present invention is approximately less than 3.6 °F (2 °C).

15 The amount of idling agent required to deactivate the active catalyst to the desired state of inactivity is based primarily on the amount of catalyst (and cocatalyst, if present), more specifically, the amount of active catalyst (e.g., transition metal in the case of a transition metal catalyzed polymerization) and cocatalyst (e.g., trialkylaluminum), if present, existing in the process and on the 20 degree to which deactivation is desired. A fraction of the stoichiometric amount of idling agent is added based on a ratio of the moles of idling agent to the moles of transition metal present in the process. Different catalysts require different ratios, but in every case the molar ratio of idling agent to the transition metal is less than the stoichiometric amount. In addition, different idling agents can 25 provide different levels of reaction suppression based on the effects of the idling agent on the active catalyst sites within the reactor. The ordinary artisan, in possession of the present disclosure, can determine the appropriate idling agent and amount of idling agent to add to a specific reaction, without undue

experimentation.

The process according to the present invention for the temporary idling of the reactor can be achieved without modifying significantly the polymerization conditions in the reactor by addition of the appropriate idling agent. Preferred 5 idling agents for a typical olefin polymerization using a fluid bed reactor are Lewis bases, such as carbon dioxide, carbon monoxide, water, oxygen, and mixtures of Lewis bases, more preferably carbon monoxide, carbon dioxide, or a mixture thereof.

A specific example of the use of the invention will now be explained in 10 detail with reference to a particular fluidized bed process, but it will be understood that it is more broadly applicable to any reaction using a catalyst, co-catalyst, or other activator which may be deactivated. It is applicable more particularly to supported catalysts and also to homogeneous catalyst systems, and can be used in gas phase, liquid phase, slurry phase, and the like.

15 In the preferred embodiment of the invention, the process of idling a reaction involves the continuous polymerization of olefins in a fluidized bed reactor. Referring to Figure 1 there is illustrated a conventional fluidized bed reaction system for polymerizing olefins. The reactor 9 consists of a reaction zone 10 and a gas velocity reduction zone 2.

20 The reactor zone 10 contains the fluidized bed of enlarging polymer particles and a minor amount of catalyst being fluidized by gas flow comprising of make-up feed stream 12 and recycle gas through the reaction zone. To maintain a viable fluidized bed, the mass gas flow rate through the bed is normally maintained above the minimum flow required for fluidization, and 25 preferably from about 1.5 to about 10 times  $G_{mf}$  and more preferably from about 3 to 6 times  $G_{mf}$ .  $G_{mf}$  is used in the accepted form as the abbreviation for the minimum gas flow required to achieve fluidization, C.Y. Wen and Y.H. Yu, "Mechanics of Fluidization", Chemical Engineering Progress Symposium Series,

- 9 -

Vol. 62, p. 100-101 (1966).

The appropriate catalyst used in the fluidized bed is preferably injected into the reactor by stream 7 with the use of an inert gas, such as nitrogen.

Catalyst concentration in the bed is substantially equal to the catalyst 5 concentration in the product, for example on the order of about 0.005 to 0.5 percent of bed volume (0.0001-0.00001 % by weight) depending on the productivity of the particular catalyst in use.

Make up monomers, stream 12, are fed to the loop at a rate approximately equal to the rate at which polymer product is withdrawn, stream 8, from the 10 reactor. The composition of the make up gas is determined by gas analyzers on the reactor recycle gas loop. From the gas analyzers, components can be fed into the make up gas to achieve the desired gas compositions.

To insure complete fluidization, the recycle gas and make up gas are returned to the base of the reactor through the gas distribution plate 1, which also 15 supports the resin bed when gas flow is stopped. The gas which does not react with the bed in the reaction zone becomes the recycle gas and passes through the velocity reduction zone such that entrained particles can return to the bed. The recycle gas is then circulated by a compressor 4 through two heat exchangers 3 and 6 in series to remove the heat of reaction absorbed from the bed before 20 returning the gas to the bed. The compressor is located between the two heat exchangers.

In addition to polymerizable olefin, hydrogen as a component in the gas stream provides a chain transfer agent for polymerization reactions. Also, any inert gas to the catalyst and reactants can also be present in the gas stream.

25 It is well known that the fluid bed reactor temperature is preferably maintained below the sintering temperature of the polymer particles. For the production of ethylene polymers, generally an operating temperature between 30 °C to 120 °C) should be maintained.

Reactor pressure can be operated at pressures of up to 1000 psig (70.0 bar), and preferably 150 to 400 psig for this particular embodiment, with operation at the higher pressures in such ranges favoring heat transfer since an increase in pressure increases the unit volume heat capacity of the gas.

5 Under a particular set of operating circumstances, the polymer withdrawal stream 8 removes polymer from the reactor at a rate equal to the production of polymer in the reactor, such that the bed level of the fluidized bed is maintained at a constant level.

Traditional Ziegler Natta catalysts typically used in the art comprise a  
10 transition metal halide, such as titanium or vanadium halide, and an organometallic compound of a metal of Group 1, 2, or 3, typically trialkylaluminum compounds (typically referred to hereinafter as "alkyl"), which serve as an activator for the transition metal halide. Some Ziegler Natta catalyst systems incorporate an internal electron donor which is complexed in the alkyl  
15 aluminum or the transition metal. The transition metal halide may be supported on a magnesium halide or complexed thereto. This active Ziegler Natta catalyst may also be impregnated onto an inorganic support such as silica or alumina. This active Ziegler Natta catalyst may also be pre-reacted to a certain degree under appropriate conditions to form a modified catalyst referred to as prepolymer,  
20 prior to the introduction to the main fluidized bed reactor.

In order to idle polymerization of a polyolefin process, it is preferred to stop catalyst injection and, if being used, co-catalyst (e.g., trialkylaluminum) injection into the reactor (as used hereinafter, the term "catalyst" is mean to include co-catalyst, when present). Stopping these feeds to the reaction process  
25 will not stop polymerization immediately if all other process parameters such as, temperature, pressure, reactor gas composition, reactor gas velocity, etc. are held constant, since active catalyst, which is still present in the reactor, continues to react with the available monomer. This deactivation step could last for a

- 11 -

considerable amount of time.

Therefore, to effectively reduce the polymerization in a short period of time while maintaining all other process parameters, a catalyst idling agent is injected into the reaction process gas.

5 Without being bound to any particular theory for the function and efficacy of the invention, the inventors believe there are two general types of deactivating agents that deactivate catalyst activity. The first type is referred to as an irreversible idling or deactivating agent. The irreversible idling agent irreversibly eliminates the ability of the catalyst to react with olefins. The polymerization 10 process will not proceed without addition of fresh catalyst. Water and oxygen are typical idling agents of the irreversible form.

The second type, which is preferred for this invention as an idling agent, is referred to as a reversible idling or deactivating agent. Carbon monoxide and carbon dioxide are typical idling agents of the reversible form. These idling 15 agents usually inhibit active catalyst sites which prevent polymerization for a limited time under normal reaction conditions. Although addition of fresh catalyst is preferred to re-establish operating conditions, some product may be produced as the reversible idling agents come off the catalyst active sites.

In the process according to the present invention, once the catalyst feed 20 (and alkyl feed if present) has been stopped, a predetermined amount of a specific idling agent is injected into the process, preferably into the gas loop upstream of the fluidized bed which prevents active catalyst sites from reacting further with the olefin which, in turn, limits polymerization to the desired rate. Again, the amount of idling agent necessary can be determined by the ordinary artisan 25 without undue experimentation, since the amount of catalyst is known by, for instance, the knowledge of the amount of catalyst in the product along with the bed volume. Thus, the amount of idling agent to add is "predetermined".

Furthermore, if alkyl addition was present prior to the injection of the

idling agent, a certain amount of the idling agent will react with the alkyl. Therefore, a greater amount of idling agent must be added to compensate for the scavenging effect of the alkyl if the desired amount of active catalyst sites are to be deactivated.

5 In contrast with technologies that utilize an agent to completely kill the reaction to prevent sintering the reactor bed in case or recycle gas compressor failure or technologies that utilize an agent to transition from one catalyst to the other, this process in the present invention allows the reaction process to be temporarily idled and to be restarted at any desired time producing product with  
10 the desired properties.

Because the invention works by reducing reaction rates, the invention is particularly applicable to all types of polyolefin fluidized bed reactors, although one of skill in the art will recognize that the invention is more broadly applicable to any polymerization reaction using a catalyst system that can be  
15 deactivated, such as a polyester reaction, reactions in solution, etc. The level of successful idling of the reactor obtained will depend on the type of catalyst system in use, including any inorganic support structure such as MgCl<sub>2</sub> or silica, but the general utility of the invention results from the interaction of the catalyst with the idling agent.

20 In a preferred embodiment, the present invention is applicable to polyethylene fluidized bed reactors, and even more preferably applicable for polyethylene fluidized bed reactors using a Ziegler Natta catalyst with a MgCl<sub>2</sub> support.

In the more preferable embodiment, it is still more preferable that the  
25 idling agent is added to the reactor gas loop. The idling agent used in the process according to the present invention can be any catalyst deactivating agent with the catalyst system in use, but in the more preferred embodiment of a polyethylene fluidized bed reactors using a Ziegler Natta catalyst with a MgCl<sub>2</sub> support, it is

- 13 -

preferred that carbon monoxide, carbon dioxide, or a mixture thereof, be used as the idling agent.

The extent of reaction suppression of different idling agents on different catalyst systems must be determined for each particular case. For a polyethylene fluidized bed reactor with a Ziegler Natta, titanium halide,  $MgCl_2$  supported catalyst system, the preferred ratio of carbon monoxide idling agent, to the titanium in the catalyst that provides adequate reaction suppression is in the range of 0.00366 to 0.0684 mole/mole of Ti, preferably 0.02 to 0.045 mole/mole Ti, most preferably about 0.038 mole/mole Ti. Thus, it can be seen that for a typical fluidized bed process using a transition metal catalyst, the amount of idling agent necessary will be less than 1 percent, on a mole/mole basis, of the amount of catalyst in the system.

According to the preferred embodiment of the present invention, the idling agent can be injected anywhere along the gas loop recycle line. More, preferably, a quicker response results when the injection is located after the second gas recycle heat exchanger 6 and directly below the distribution plate is most preferred.

As used herein, the term ethylene polymers, ethylene copolymers, or polyethylene also includes copolymers composed of ethylene and one or more other olefins (comonomer). These other olefins are preferably alpha-olefins. Also included in this definition of polymers are terpolymers of ethylene and two or more comonomers. Examples of suitable alpha-olefins include, but are not limited to, propylene, butene-1, pentene-1, hexene-1, 4-methylpentene-1, and octene-1, with hexene-1, 4-methylpentene-1, and butene-1 being most preferred.

Key elements in the reactor loop for a preferred embodiment of the reactor are illustrated in Figure 1 and include reactor vessel 9, heat exchangers 3 and 6, compressor 4, and gas distributor plate 1.

The following examples are intended to illustrate the present invention.

Numerous modifications and variations will suggests themselves to those of skill in the art, and it is to be understood that the invention may be practiced otherwise than as specifically described herein.

5    Example 1

A conventional gas phase fluidized bed polyethylene reaction process such as disclosed in U.S. Patent No. 5,332,706 (incorporated herein by reference) is utilized and which is modified as shown in Figure 1. A conduit for introducing 100% carbon monoxide gas at a pressure of approximately 900 psig (63.1 bar) from a cylinder opens into the recycle conduit at a distance 10 feet (3.05 m) from the reentry in the lower part of the reactor.

Above the distribution plate in the reactor contains a fluidized bed consisting of linear low density polyethylene powder. The reaction gas mixture, 15 67% by volume of nitrogen, 25% of ethylene, 4% of hydrogen, and 4% of 1-hexene, flows through the fluidized bed at a pressure of 300 psig (21.7 bar), at 183 °F (84 °C) and with an upward fluidization velocity of 1.7 ft/s (0.518 m/s).

In an incident where temperature in part of the bed reached approximately 212 °F (100 °C), idling operation begins by immediately stopping catalyst injections into the reactor. Simultaneously, the measured amount of carbon 20 monoxide gas contained in the conduit was introduced in the reactor in less than 30 seconds, in a quantity of 0.038 mole per mole titanium, by dropping the pressure in the conduit from 900 psig (63.1 bar) to 300 psig (21.7 bar). It was discovered that the reaction idled within 15 minutes with a reactor bed temperature differential, approximately 3.6 °F (2 °C), and without any 25 detrimental effects, i.e. producing large agglomerates. The reactor pressure was maintained at 300 psig (21.7 bar) and the gas compositions were also maintained at conditions prior to injection.

Under these conditions, the polymerization reaction was restarted upon the

introduction of fresh catalyst, without the addition of a catalyst activator and/or poison scavenger, without having to drain the bed and even without having to purge the reaction gas mixture from the reactor.

5      Example 2

The reactor operation is carried out under conditions which are identical with those given in Example 1.

A different incident occurs where the powder withdrawal system experiences pluggages that prevent the removal of polymer powder from the 10 reactor. The idling operation is carried out the same way as in Example 1 to prevent the fluidized bed to reach the high levels where the bed begins to carryover into the gas recycle stream. The reaction idled within 15 minutes with a reactor bed temperature differential, approximately 3.6 °F (2 °C), and without any detrimental effects, i.e. producing large agglomerates. The reactor pressure 15 and gas compositions were maintained at conditions prior to injection and the fluidized bed level remained constant. The reaction was restarted in the same manner as in Example 1.

The above examples clearly illustrate that an idling agent can be added to deactivate a catalyst involved in a polymerization process in a predetermined 20 amount so that the polymerization process can be immediately restarted solely by introduction of fresh catalyst.

The invention has been described above in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications other than as specifically described herein can be effected within the 25 spirit and scope of the appended claims. Moreover, all patents and literature references or other publications noted above are incorporated herein by reference for any disclosure pertinent to the practice of the invention.

CLAIMS

1. In a polymerization process including a catalyst, a process for reducing the reaction rate of the polymerization process by adding a catalyst deactivator, the  
5 improvement comprising adding an deactivating agent in an amount less than the stoichiometric amount necessary to deactivate the catalyst, so that the polymerization process can be re-established solely by adding fresh catalyst.
2. The process according to Claim 1, wherein the polymerization process  
10 occurs in a fluidized gas phase reactor.
3. The process according to Claim 2, wherein the polymerization process occurs in a low pressure gas phase fluidized bed reactor.
- 15 4. The process according to Claim 1, wherein the polymerization process includes the polymerization of olefins.
5. The process according to Claim 2, wherein the polymerization process includes the polymerization of olefins.  
20
6. The process according to Claim 1, wherein the catalyst includes titanium.
7. The process according to Claim 2, wherein the catalyst includes titanium.
- 25 8. The process according to Claim 1, wherein the reaction is reduced 85 % to 99 % from the production prior to addition of the deactivating agent.
9. The process according to Claim 5, wherein the catalyst includes titanium.

10. The process according to Claim 1, wherein the deactivating agent is a Lewis base.
- 5     11. The process according to Claim 1, wherein the deactivating agent is selected from the group consisting of carbon monoxide, carbon dioxide, water, oxygen, and mixtures thereof.
- 10     12. The process according to Claim 1, wherein the deactivating agent is selected from the group consisting of carbon monoxide, carbon dioxide, and mixtures thereof.
- 15     13. The process according to Claim 5, wherein the deactivating agent is selected from the group consisting of carbon monoxide, carbon dioxide, and mixtures thereof.
- 20     14. The process according to Claim 13, wherein catalyst is titanium and the deactivating agent is present in the amount of 0.00366 to 0.0684 moles per mole of titanium.
- 25     15. The process according to Claim 1, said polymerization process comprising the production of polyolefins and including the continuous addition of fresh catalyst, wherein process of reducing the rate consists essentially of stopping fresh catalyst feed and adding said deactivating idling agent, without any change in temperature or pressure of the reactor, and further including an additional step of re-establishing the production of polyolefins, said additional step consisting essentially of adding fresh catalyst.

- 18 -

16. A process for idling a reactor process, wherein said reactor process includes a catalyst, comprising adding an idling agent to the reactor in an amount just sufficient to idle the reactor process, whereby said reactor process can be re-established solely by adding fresh catalyst.

5

17. The process according to Claim 16, wherein the moles of idling agent added is less than the moles of active catalyst present.

10

18. The process according to Claim 16, wherein the idling agent is a Lewis base.

10

19. The process according to Claim 16, comprising the polymerization of olefins in a low pressure gas phase fluidized bed reactor, wherein the catalyst includes a transition metal catalyst selected from titanium and vanadium.

15

20. The process according to Claim 19, wherein the idling agent is selected from the group consisting of carbon dioxide, carbon monoxide, water, oxygen, and mixtures thereof.

20

21. The process according to Claim 20, wherein the idling agent is selected from the group consisting of carbon monoxide, carbon dioxide, and mixtures thereof.

22. The process according to Claim 21, wherein the transition metal is titanium and the idling agent is present in the amount of from 0.00366 to 0.0684 moles per mole of titanium.

25

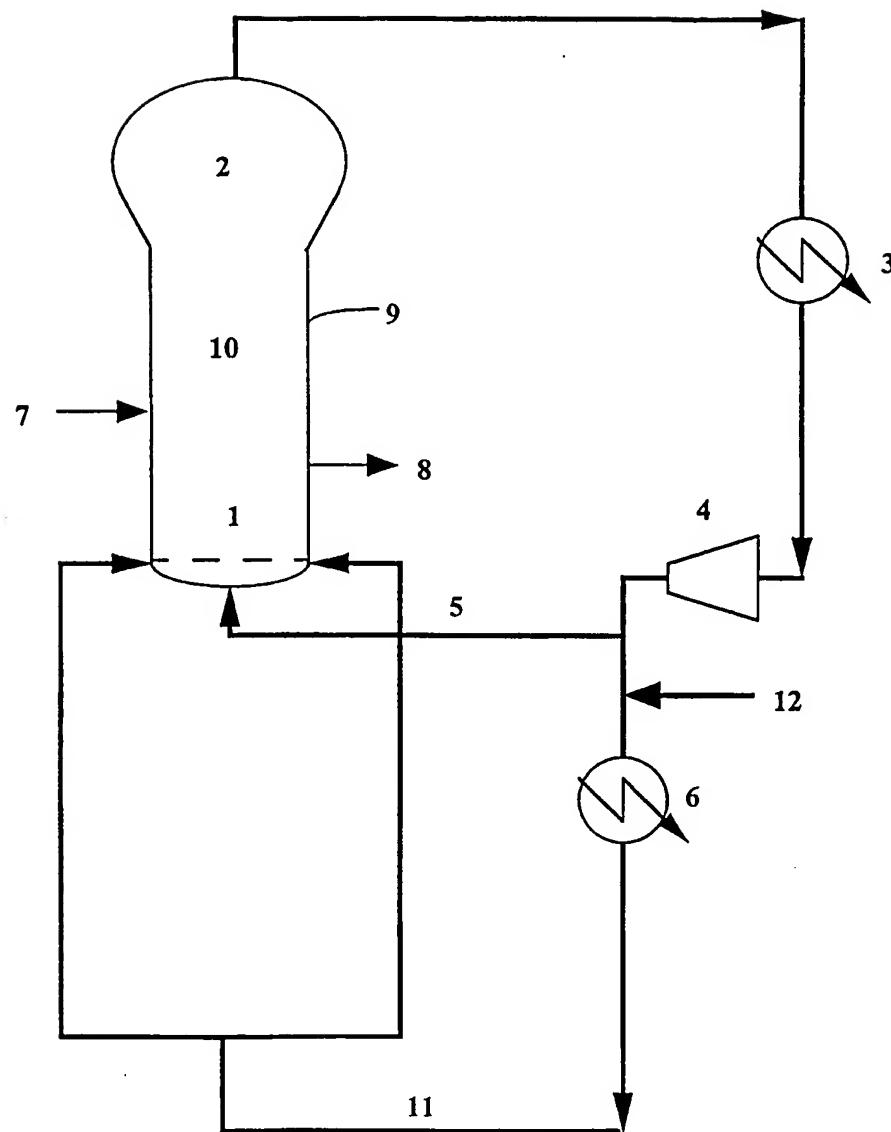
23. The process according to Claim 16, wherein the reaction is idled 85% to 99% from the production prior to addition of the idling agent.

- 19 -

24. The process according to Claim 16, further comprising the step of re-establishing the reaction by a step including the addition of fresh catalyst.
- 5 25. The process according to Claim 21, further comprising the step of re-establishing the reaction by a step including the addition of fresh catalyst.
26. The process according to Claim 16, further comprising the step of re-establishing the reaction by a step consisting essentially of adding fresh catalyst.
- 10 27. The process according to Claim 21, further comprising the step of re-establishing the reaction by a step consisting essentially of adding fresh catalyst.

1/1

Figure 1



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/00553

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08F2/42 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 630 910 A (UNION CARBIDE CHEM PLASTIC) 28 December 1994  see abstract see example 1, figure 1 and table I : example 20 see example 28 see page 7, line 18 - line 22 see page 8, line 21 - line 41 see claims 7,9 ---	1,4,8, 10,11, 15,16, 18,23, 24,26  2,5
X	US 5 200 502 A (KAO SUN-CHUEH ET AL) 6 April 1993  see example 30 see examples 23,24 see example 30 ---	1-5  6,8,10 14
A		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
---	--

22 April 1998

07/05/1998

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Gamb, V

## INTERNATIONAL SEARCH REPORT

Int'l. Application No

PCT/US 98/00553

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 414 063 A (SEEGER HORST K ET AL) 9 May 1995  see column 5, line 27 - line 31 see column 7, line 51 - line 54 see example 4 -----	1,2,4-7, 9,10,15, 16,18, 24,26

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l. Appl. No.

PCT/US 98/00553

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0630910 A	28-12-94	AU 6596694 A BR 9402553 A CA 2126796 A JP 7025925 A		05-01-95 28-03-95 29-12-94 27-01-95
US 5200502 A	06-04-93	AT 135018 T AU 666207 B AU 4486993 A BR 9303478 A CA 2104843 A,C CN 1088220 A DE 69301703 D DE 69301703 T EP 0585796 A ES 2084427 T JP 6184231 A MX 9305160 A ZA 9306230 A		15-03-96 01-02-96 03-03-94 22-03-94 27-02-94 22-06-94 11-04-96 08-08-96 09-03-94 01-05-96 05-07-94 31-05-94 21-03-94
US 5414063 A	09-05-95	JP 6298831 A		25-10-94